

# IMPROVED STEEL SURFACE HARDNESS USING LASER DEPOSITION AND ACTIVE GAS SHIELDING

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## STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

The United States Government has rights in this invention pursuant to contract no.  
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Battelle, LLC.

## FIELD OF THE INVENTION

15 The present invention relates generally to laser metal deposition methodology for  
making hard surface steel alloys. More particularly, it relates to making high-hardness  
steel surfaces and improved control of bead contours by the use of active nitrogen  
shielding together with laser surface alloying of premixed steel powders and carbide  
powders on a steel surface.

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## BACKGROUND OF THE INVENTION

Laser surface alloying (LSA) is a versatile process through which one can modify  
the surface properties of metals and ceramics to obtain required properties. The  
25 properties of the surface are modified by localized melting and solidification. The LSA  
process alters the solidified microstructure by alloy-induced transformations, composite  
strengthening through the production of a coating comprised of a matrix material and  
second-phase particles, or a combination of both. The most common uses are for  
improving resistance to corrosion, abrasion, erosion, oxidation, and wear (1).

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Current LSA processing of steel surfaces relies on choosing the laser power and modifying the material characteristics to produce harder surfaces. The addition of alloying elements to the molten pool modifies the liquid pool composition. The alloying elements are added by pre-placing powders on the substrate, pre-blending the matrix powder and hard particles and feeding directly into the laser beam and material interaction region, or by injecting the hard particles into the trailing edge of the molten pool. Some processes have also combined the various methods for providing the powder additions, as well as the use of solid wire for the matrix material. In all cases, LSA processing of steel has been performed with inert gas shielding using argon or helium to avoid contamination by oxygen and nitrogen.

Recently, 100% nitrogen shielding was used in laser surface alloying of titanium alloys to produce harder titanium surfaces (2). Such a nitrogen shield process cannot be extended to steels, however, since it is well known that excess amounts of nitrogen dissolution into liquid steel will lead to gas porosity (3). No use of nitrogen shielding for laser surface alloying of steels is known prior to this invention.

We have carefully modified the shielding gas composition, hard particle powder composition, laser surface alloying process parameters, and matrix powder composition in order to achieve harder steel alloy surfaces and better bead formation on steel surfaces.

## REFERENCES

1. S. S. Babu et. al., "Toward Prediction of Microstructural Evolution during Laser Surface Alloying", Metallurgical and Materials transactions A, Vol. 33A, pp. 1189-1200, (2002).
2. I. Garcia, et. al., "(Ti,Al) / (Ti,Al)N Coatings Produced by Laser Surface Alloying", Materials Letters, Vol. 53, pp. 44-51, (2002).
3. S. Kou, "Welding Metallurgy", John Wiley & Sons, New York, p. 64, (1987).

## OBJECTS OF THE INVENTION

It is an object of this invention to modify the gas shielding used with steel alloy  
5 laser surface alloying processes to allow excess nitrogen to enter the liquid steel.

It is another object of this invention to utilize alloying elements in a steel alloy  
laser surface alloying process such that the alloying elements will dissolve in the liquid  
steel and react with dissolved nitrogen to form fine hard particles before the onset of  
10 solidification of the steel matrix.

It is another object of this invention to select laser surfacing process parameters in  
a steel alloy laser surface alloying process that will allow for dissolution of particles,  
dissolution of nitrogen from a shielding gas and also provide the proper cooling rate to  
15 allow for re-precipitation of fine hard particles.

It is a further object of this invention to select a matrix composition in a steel  
alloy laser surface alloying process that does not adversely influence the dissolution and  
re-precipitation of hard particles.  
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Further and other objectives of the present invention will become apparent from the  
description contained herein.

## SUMMARY OF THE INVENTION

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In one embodiment, the invention is a method of controlling bead shape in a steel  
alloy laser deposition process comprising laser melting an addition of titanium carbide  
powder and steel powder mixture to a steel surface using a shielding gas comprising 1 %  
to 100 % nitrogen. The shielding gas can further comprise an inert gas and/or air.

In another embodiment, the invention is a method of controlling bead shape in a steel alloy laser deposition process comprising laser melting an addition of material comprised of titanium carbide and steel on a steel surface in air.

5           In a further embodiment, the invention is a method for producing a high-hardness steel surface comprising the steps of: introducing an addition of a powder mixture containing 10 to 60 weight percent titanium carbide powder and the balance steel onto a steel surface by preplacing the mixture on the surface, feeding the mixture into the interaction area, or combining the preplacing and feeding of the addition components;  
10       laser melting the powder additions and a relatively small amount of the steel surface using 1 % to 100 % nitrogen as shielding gas; and cooling at a rate such that a steel surface with fine titanium carbonitride particles is formed.

#### BRIEF DESCRIPTION OF THE DRAWINGS

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Fig. 1a is a photomicrograph of laser bead made on a 431 martensitic steel powder with argon shielding of 20 cfh.

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Fig. 1b is a photomicrograph of laser bead made on premixed 431 martensitic steel and 20% TiC powders with argon shielding of 20 cfh.

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Fig. 1c is a photomicrograph of laser bead made on premixed 431 martensitic steel and 20% TiC powder with mixture of 18 cfh of argon and 2 cfh of nitrogen as shielding gas.

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Fig. 1d is a photomicrograph of laser bead shape made on premixed 431 martensitic steel and 20% TiC powders in air.

Fig. 1e is a photomicrograph of laser bead shape made on premixed 431 martensitic steel and 20% TiC powder with nitrogen shielding of 20 cfh.

Fig. 1f is a comparison of bead outline showing the effect of gradually increasing nitrogen content on the bead shape.

Fig. 2a. is a high magnification optical photomicrograph of laser bead made on  
5 431 martensitic steel powders with argon shielding of 20 cfh.

Fig. 2b. is a high magnification optical photomicrograph of laser bead made on  
premixed 431 martensitic steel and 20% TiC powder with argon shielding of 20 cfh.

10 Fig. 2c. is a high magnification optical photomicrograph of laser bead made  
on a premixed 431 martensitic steel and 20% TiC powder with shielding made with  
mixture of 18 cfh of argon and 2 cfh of nitrogen.

Fig. 2d. is a high magnification optical photomicrograph of laser bead made on a  
15 premixed 431 martensitic steel and 20% TiC powder with shielding made in air with no  
intentional shielding.

Fig. 2e. is a high magnification optical photomicrograph of laser bead made on  
premixed 431 martensitic steel and 20% TiC powder with nitrogen shielding of 20 cfh.  
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Fig. 3a is the measured hardness distribution image of laser bead made on 431  
martensitic steel powders with argon shielding of 20 cfh.

Fig. 3b is the measured hardness distribution image of laser bead made on  
25 premixed 431 martensitic steel and 20% TiC powders with argon shielding of 20.

Fig. 3c is the measured hardness distribution image of laser bead made on  
premixed 431 martensitic steel and 20% TiC powders with shielding made with mixture  
of 18 cfh of argon and 2 cfh of nitrogen.  
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Fig. 3d is the measured hardness distribution image of laser bead made on premixed 431 martensitic steel and 20% TiC powders with shielding made in air with no intentional shielding.

5            Fig. 3e is the measured hardness distribution image of laser bead made on premixed 431 martensitic steel and 20% TiC powders with nitrogen shielding of 20 cfh.

Figure 4 is the comparison of hardness distributions in the laser deposits made with different conditions.

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Figure 5 is the comparison of average hardness of the laser deposits for various conditions.

#### DETAILED DESCRIPTION OF THE INVENTION

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In this laser surface alloying process, harder surface coatings are produced in a laser metal deposition process carried out using active nitrogen shielding and by adding titanium carbide (TiC) particles in a steel matrix. In particular, the harder surface compounds are formed by reaction of the dissolved titanium, carbon and nitrogen which forms harder particles in a steel matrix. Inert gas shielding can be eliminated while yielding better hardness and providing control over the bead shape.

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A mild steel of 1020 type was chosen as the substrate for the experimentation. The matrix was designed to be of type 431 martensitic steel composition. The specifications are given in Table 1. The types of hard particle powders used in the experimentation include titanium carbide (TiC), titanium nitride (TiN) and standard tungsten carbide (WC) powders. The specifications of TiC and TiN powders are given Table 1.

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Table 1: Specifications of 431 steel and TiC and TiN powders

431 Powder	Sulzer Metco 42C powder, commercial 431 alloy purity, size -325+80 size, and lot number W53351
TiC Powder	AEE Corporation, 99.9% purity, size estimated at -325+150, and lot number CAS-7440-33-7.
TiN Powder	Alfa Products Corporation, 99% purity, size estimated at -325+150, and lot number 031986.

5           The laser deposition was made in a Hobart Model HLP 3000 3.0 kW Nd:YAG laser with fiber optic beam delivery and f16 focus optics. A laser power of 2430 W was used in all experiments. The energy absorption for this experimental setup at 2 mm powder thickness was approximately 70%. In all the experiments the powder material to be melted by laser process was premixed and preplaced on the substrate surface. The  
10 width of the powder layer was 0.20 inches. The thickness of the powder layer was 0.08 inch.

          The details of the experimental conditions used in the experiments are given in Table 2. The laser bead shape and microstructure in the coatings were characterized  
15 using optical microscopy after standard etching. The hardness distributions in the coatings were measured with an automated hardness tester with 300 and 500 g loads and are given in terms of Vickers Hardness Number (HV). See FIGS. 4 and 5.

          A laser bead with 431 steel powders alone and with argon shielding at 20 cubic  
20 feet per hour (cfh) was made first. The laser bead shape (see FIG. 1a) shows extensive melting of the substrate compared to other conditions.

          Mixing 20% by weight of TiC powders to the 431 steel powders (see FIG. 1b) and with argon shielding at 20 cfh led to reduction in the size of the bead. In addition, the

liquid metal flow over the substrate sides was reduced compared to the bead with no TiC additions.

5 In the next run, a small amount of nitrogen was mixed with argon shielding. This was done by mixing 2 cfh of nitrogen with 18 cfh argon. This led to smoother and smaller bead shape (see FIG. 1c) compared to the previous conditions.

To evaluate the effect of increasing nitrogen, the shielding was completely removed and the effect of ambient air present during laser bead deposition was tested.  
10 The bead shape (see FIG. 1d) was again smaller than previous conditions. However, the surface was rougher compared to previous conditions. This may have been due to oxygen contamination from the air.

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Table 2. Experimental matrix used in the investigation to evaluate the effect of nitrogen, air and argon shielding with carbide and nitride particles

Base Metal	1020 Mild Steel
Beam Diameter	5 mm Nd:YAG
Power	2430 W
Optics	F16 -- Fiber Optic Delivery
Laser Orientation	15° rear angle (Run#1-22)
	15° forward angle (Run#22-30)
Gas Supply	0.375" I.D. copper tube @ 30°
Powder Thickness (thoroughly mixed)	0.080" t X 2.5" L (Run#1-22)
	2.5" L (Run#22-30)

Run #	Matrix/Particle Material (% by wt)				Speed (IPM)	Shielding (cfh)		Powder Delivery	Notes
	431	TiN	TiC	WC		Ar	N <sub>2</sub>		
1	100%	-	-	-	5	20	-	preplaced	
2	100%	-	-	-	5	18	2	preplaced	
3	100%	-	-	-	5	-	-	preplaced	
4	80%	20%	-	-	5	20	-	preplaced	
5	80%	20%	-	-	5	18	2	preplaced	
6	80%	20%	-	-	5	-	-	preplaced	
7	80%	-	20%	-	5	20	-	preplaced	
8	80%	-	20%	-	5	18	2	preplaced	
9	80%	-	20%	-	5	-	-	preplaced	
10	80%	-	20%	-	15	20	-	preplaced	
11	80%	-	20%	-	15	18	2	preplaced	
12	80%	-	20%	-	15	-	-	preplaced	
13	80%	-	20%	-	15	-	20	preplaced	
14	80%	-	20%	-	5	-	20	preplaced	
15	80%	-	20%	-	15	20	-	preplaced	3 passes & 3 mm overlap
16	80%	-	20%	-	15	-	20	preplaced	3 passes & 3 mm overlap
17	100%	-	-	-	15	-	20	preplaced	
18	100%	-	-	-	5	-	20	preplaced	
19	80%	-	-	20%	5	20	-	preplaced	
20	80%	-	-	20%	5	-	20	preplaced	
21	80%	-	-	20%	15	-	20	preplaced	
22	80%	-	-	20%	15	20	-	preplaced	
23	80%	-	-	30%	5	20	-	tube-fed	reverse direction
24	80%	-	-	30%	15	20	-	tube-fed	reverse direction
25	80%	-	-	30%	5	-	20	tube-fed	reverse direction
26	80%	-	-	30%	15	-	20	tube-fed	reverse direction
27	80%	-	30%	-	5	20	-	tube-fed	reverse direction
28	80%	-	30%	-	15	20	-	tube-fed	reverse direction
29	80%	-	30%	-	5	-	20	tube-fed	reverse direction
30	80%	-	30%	-	15	-	20	tube-fed	reverse direction
31	50%	-	50%	-	5	20	-	tube-fed	reverse direction

In the next run, 100% nitrogen was used as a shielding gas by making the laser beads with 20 cfh flow of nitrogen around the bead region. The bead shape attained with this condition is shown in FIG. 1e. Since there was no oxygen contamination in this experiment, the bead was much smoother. Interestingly, the bead was smaller than in  
5 previous runs.

A comparison of the outlines from all the laser beads is shown in FIG. 1f. FIG. 1f shows the effect of gradually increasing the nitrogen content in the shielding gas. With the increase in nitrogen content, the weld pool shape became smaller and smaller. The  
10 results show that one can modify the bead shape by controlling the nitrogen content in the shielding gas.

The microstructures obtained in conditions 1, 7, 8, 9, and 14 (see Table 2) are shown in FIG. 2. The microstructure from condition 1 did not contain any carbide and  
15 showed only martensite matrix (see FIG. 2a). The microstructures from conditions 7 (see FIG. 2b), 8 (see FIG. 2c), 9 (see FIG. 2d), and 14 (see FIG. 2e) showed the presence of fine carbides in the form of particles and also dendritic form. The microstructure from condition 8 (see FIG. 2c) shows some coarse TiC particles which have not melted  
20 completely.

The presence of fine particles smaller than original particle size indicates that most of the original TiC powders dissolve in the liquid steel. On dissolution, the super saturation of titanium and carbon increases as well as the nitrogen due to dissolution from the shielding environment. Then, during cooling from high temperature, the dissolved  
25 titanium, carbon and nitrogen react to precipitate as titanium carbonitride, Ti(CN). The presence of dendritic shaped Ti(CN) particles indicates these precipitates are forming much before the primary solidification of the steel matrix. The carbides obtained in condition 14 were much finer. This is attributed to the higher supersaturation of nitrogen, and is also partly due to faster cooling in the deposit due to the smaller bead shape.

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The hardness distribution in conditions 1 (see FIG. 3a), 7 (see FIG. 3b), 8 (see FIG. 3c), 9 (see FIG. 3d), and 14 (see FIG. 3e) are compared in FIG. 3. The hardness distributions were measured one one-half of the cross sections shown in FIG. 1a-1e. The hardness values were measured at a spatial resolution of 200 micro-meters ( $\mu\text{m}$ ). The distributions are shown in a gray scale image format. The darker contrast indicates higher hardness and lighter contrast shows low hardness. Qualitative overview of the images showed that the condition 14 attained highest hardness.

The hardness distributions are compared in FIG. 4. The results show that the coating made with (condition 14) 431 steel powders with 20 % TiC under 20 cfh nitrogen shielding produced the maximum hardness. This result shows that by increasing the nitrogen content in the shielding the hardness of the coating can be increased.

Table 3. Measured Hardness Data in the substrate and the coatings produced in different conditions.

Run	Minimum Substrate Hardness, HV	Maximum Substrate Hardness, HV	Minimum Coating Hardness, HV	Maximum Coating Hardness, HV	Average Coating Hardness, HV
1	140.7	285.43	393.97	461.918	437.76
7	136.18	249.25	529.65	1834.78	573.69
8	172.36	244.72	579.4	1378.12	621.07
9	154.27	258.29	602.01	1007.26	637.08
14	167.84	298.99	651.76	1103.95	724.39

The average hardness of the deposits made in conditions 1, 7, 8, 9, and 14 were calculated by assuming a Gaussian distribution. The values are compared in FIG. 5 and in Table 3. The maximum hardness in the coating was occasionally above 1000 HV (see Table 3). This is attributed to sampling of coarse carbides present in the coating by the

hardness indenter. Therefore, for true representation of coating performance, the average hardness is evaluated further.

5 The average substrate hardness close to the coating did not change much in all conditions tested. A maximum hardness of 280 to 300 HV in the substrate is related to the formation of martensite in the regions close to the laser bead due to rapid cooling from the single-phase austenite region.

10 The average hardness of the coating in condition 1 was 437.76 HV. On adding 20% TiC (condition 7) lead to an increase in average hardness to 573.69 HV. This 31% increase in hardness is attributed to the addition of TiC to the deposit.

15 The average hardness of condition 8 was 621.07 HV. This 8% increase in hardness was attributed to increasing levels of dissolved nitrogen, as well as the hard Ti(CN) compound formed by reaction with the dissolved titanium and carbon.

20 The average hardness of condition 9 was 637.08 HV. This shows only a 2% increase in hardness over condition 8. Although one would expect higher levels of nitrogen dissolution in condition 9, the hardness increase was only 2%. This is attributed to deleterious effects of possible oxygen contamination.

25 The average hardness of condition 14 was 724.39 HV. This shows that 13% increase in hardness compared to condition 9 can be achieved by 100 % nitrogen shielding. Condition 8 gave a 31% increase in the hardness compared to condition 7. However, condition 14 gave a 65% increase in the hardness compared to condition 7.

30 The hardness data conclusively show that use of laser metal deposition, 431 steel powders, the addition of TiC powders and 100 % nitrogen shielding increases the surface hardness of the laser deposits.

While there has been shown and described what are at present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications can be prepared therein without departing from the scope of the invention defined by the appended claims.